

*Ford Motor Company*

**Temperature Transient Effects in  
Plasma-Catalysis  
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# Background



- Ford is working on plasma-catalysis as part of the USCAR LEP CRADA with PNNL
- Developed low temperature NO<sub>x</sub> catalysts
- Recent cooperation with Caterpillar to jointly evaluate “our” catalyst and “theirs”
- Ford data using a temperature transient test method

# Experimental



- Mass flow controllers blend simulated exhaust
- Flow system
  - Dielectric barrier discharge device in first oven
  - Catalyst(s) in second oven
  - Permits feedgas, midbed, downstream samples
  - Sample diluted 5:1 with N<sub>2</sub>; water is not removed
- Analysis by high resolution FTIR plus emission analyzer bench (CLA, FID, O<sub>2</sub>, CO, CO<sub>2</sub>)

# Thermal Cycle Testing

- Temperature ramps: 10 °C/min between about 100°C to 500°C, with 12 minute hold at each end; each cycle is 104 minutes. Both ovens ramp.
- Typically 15-20 hours cycling
- **NOT** known to correlate with real world aging!
- Gas Blend (unless noted):
  - 260 ppm NO
  - 0 or 50 ppm SO<sub>2</sub>
  - 7% CO<sub>2</sub>
  - 7% O<sub>2</sub>
  - 1% Ar
  - 1000 ppm CO
  - 333 ppm H<sub>2</sub>
  - 1500 ppm C<sub>1</sub> C<sub>3</sub>H<sub>6</sub> 7.6 C<sub>1</sub>:NO<sub>x</sub>
  - 500 ppm C<sub>1</sub> C<sub>3</sub>H<sub>8</sub>
  - 2.8% H<sub>2</sub>O

# Catalysts Tested



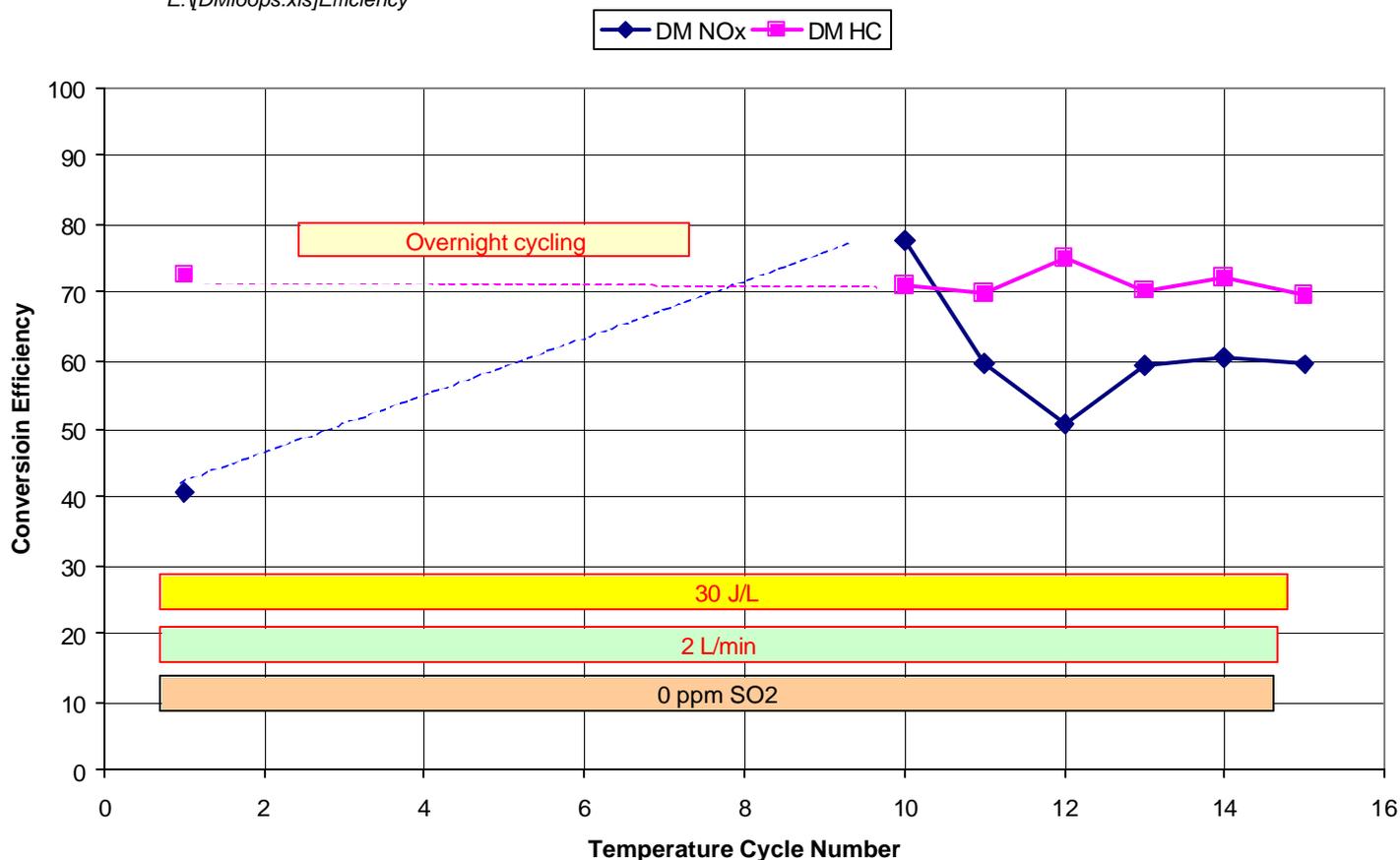
- BaY with added impregnation (BaY+)
  - Prepared by PNNL under the LEP CRADA
- Caterpillar catalyst “B”
  - Provided by Paul Park
  - Alumina based
- Combinations:
  - BaY-alumina-Pt
  - Impregnated Y - CatB (BaY+/B)

# Catalyst B Thermal Loops



DM: CatB Loop Tests

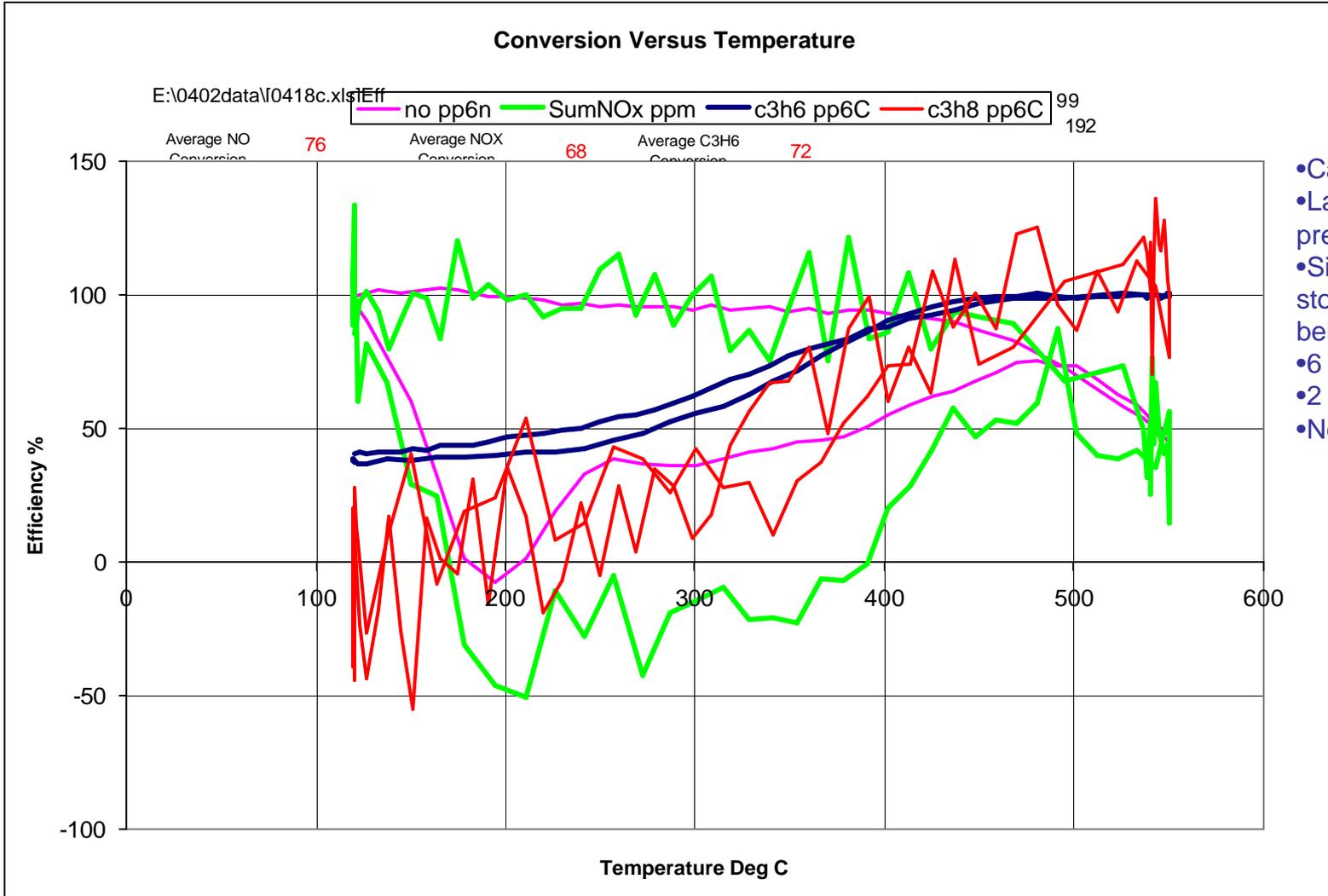
E:\DMloops.xls\Efficiency



- Alumina based "HD" catalyst
- Data integrated over temperature loops
- Data only recorded during daytime
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

# Catalyst B

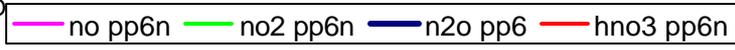
Conversion Versus Temperature



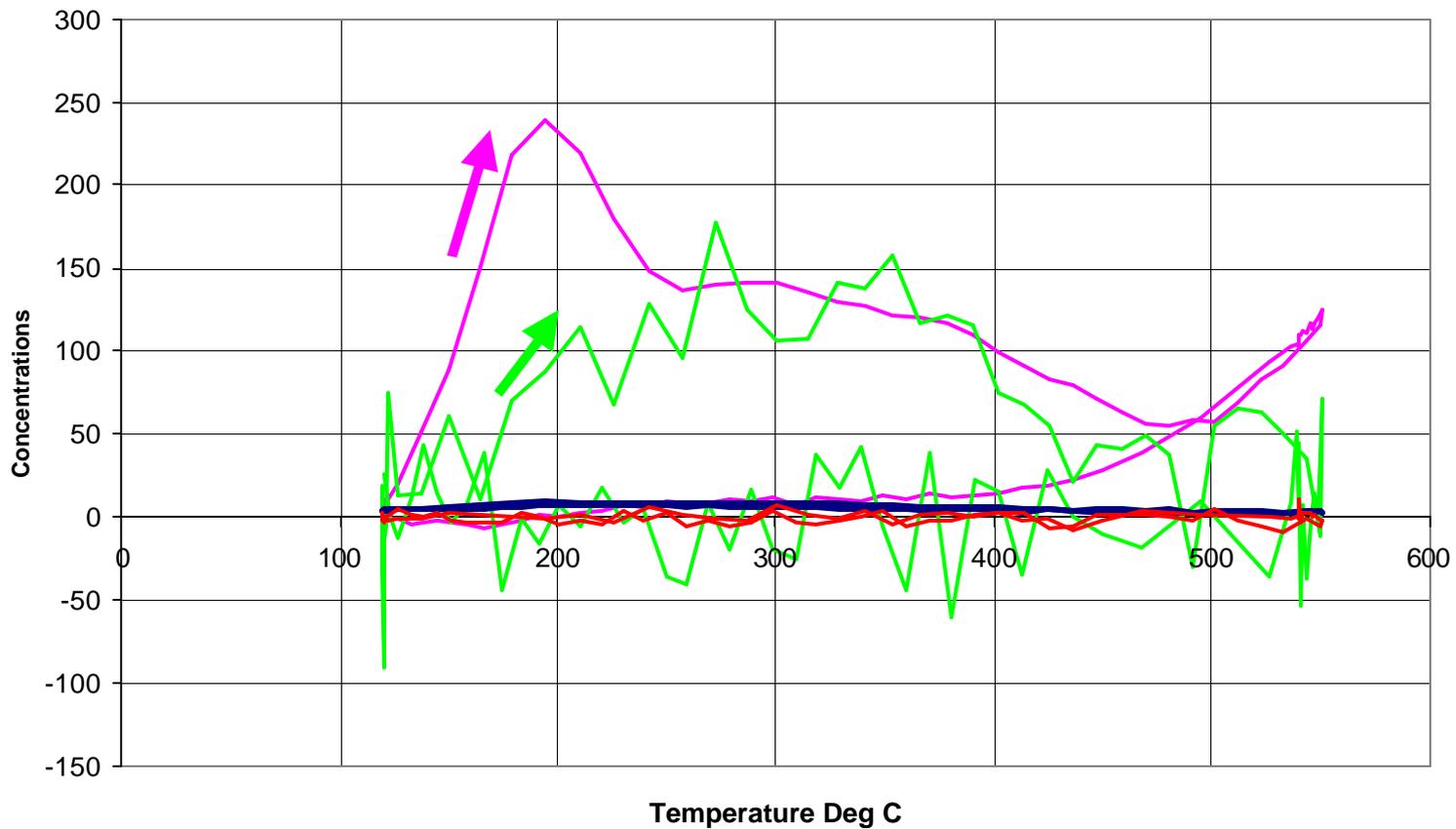
- Catalyst B
- Last loop of previous plot
- Significant NOx storage/release below 350°C
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

### NOx versus Temperature

E:\0402data\0418c.xls\NO



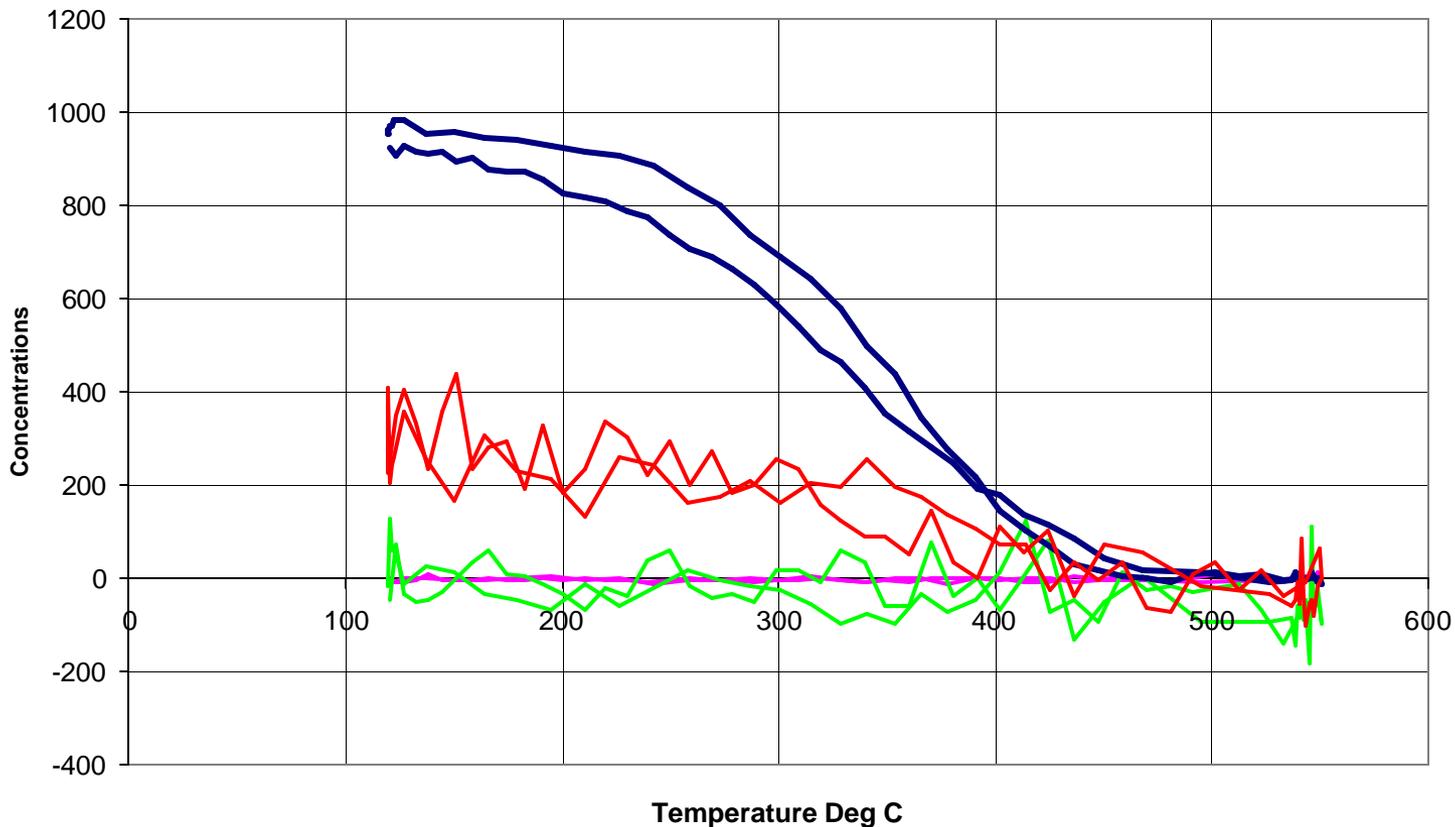
99  
19



- Catalyst B
- Last loop
- NO and NO<sub>2</sub> released during heating
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

## HC and Aldehydes versus Temperature

E:\0402data\0418c.xls]HC  
 ch2o pp6 ch3cho pp6 c3h6 pp6C c3h8 pp6C 99  
 196



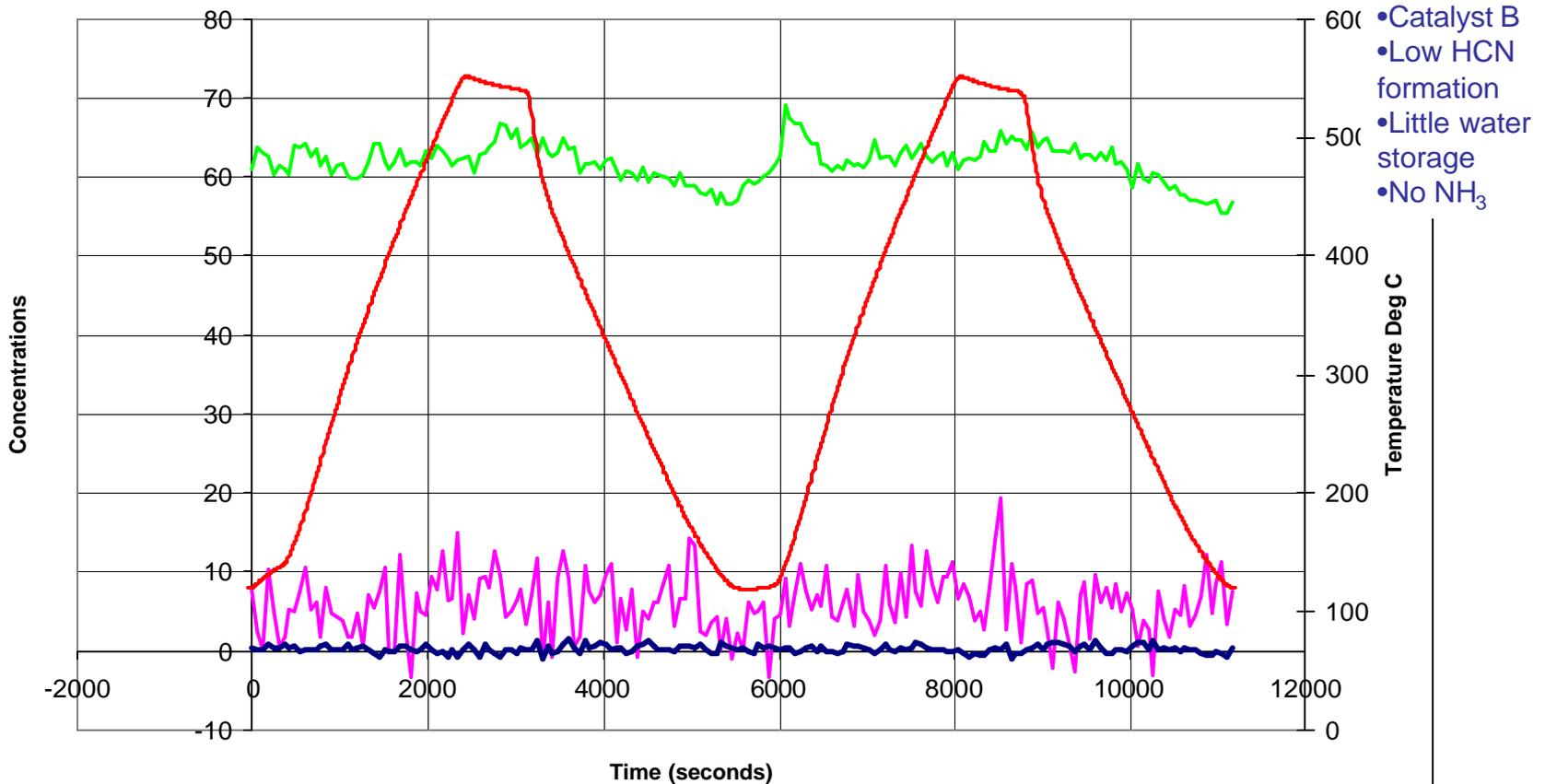
- Catalyst B
- Last loop
- Little storage of HCs
- Aldehydes consumed/stored at all temperatures
- Probably explains why "LD" catalyst needs to be in front
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

### Assorted Values Versus Time

E:\0402data\0418c.xls\Mis

hcn h2o pp3 nh3 pp6 Cat IN

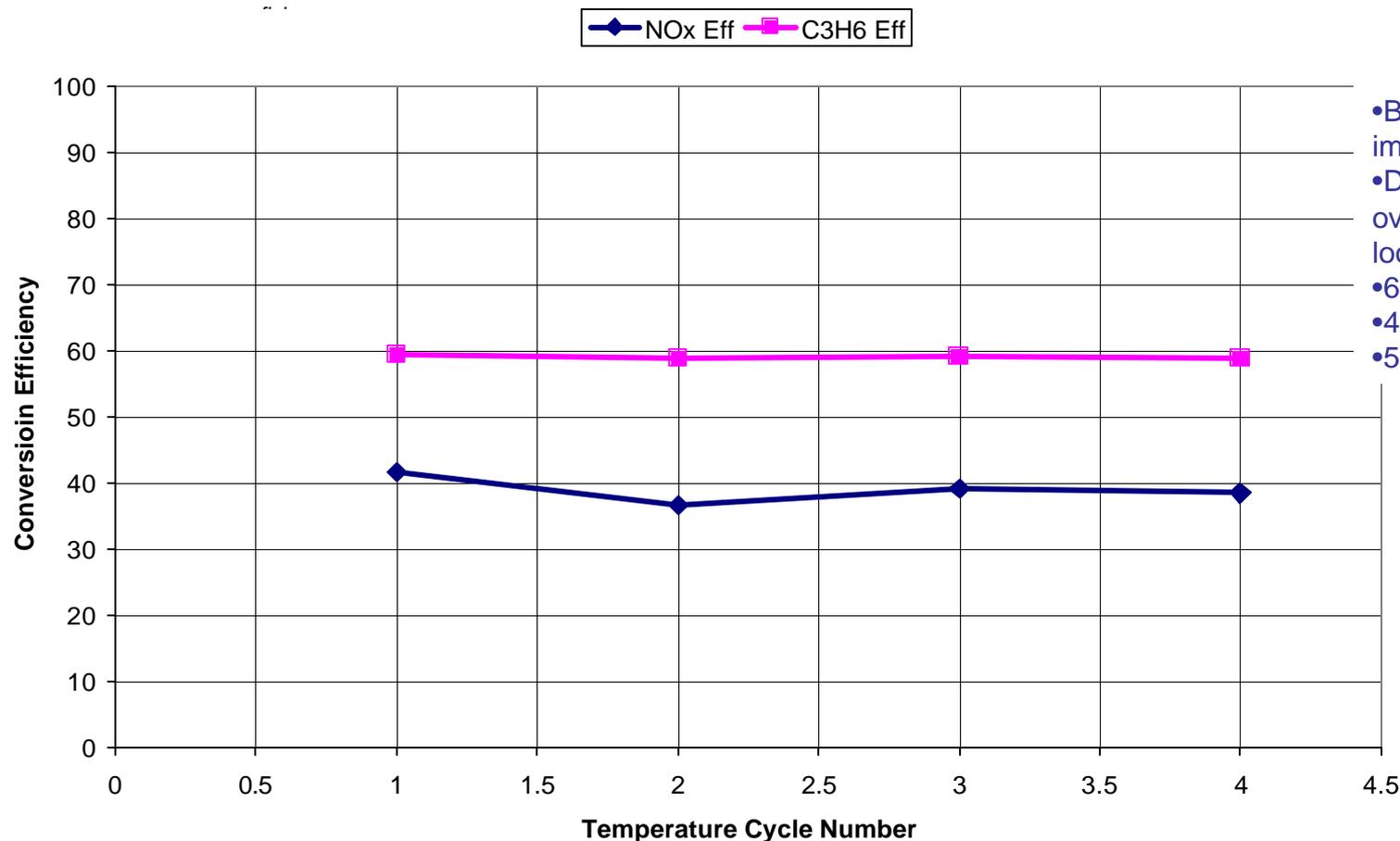
6  
1000



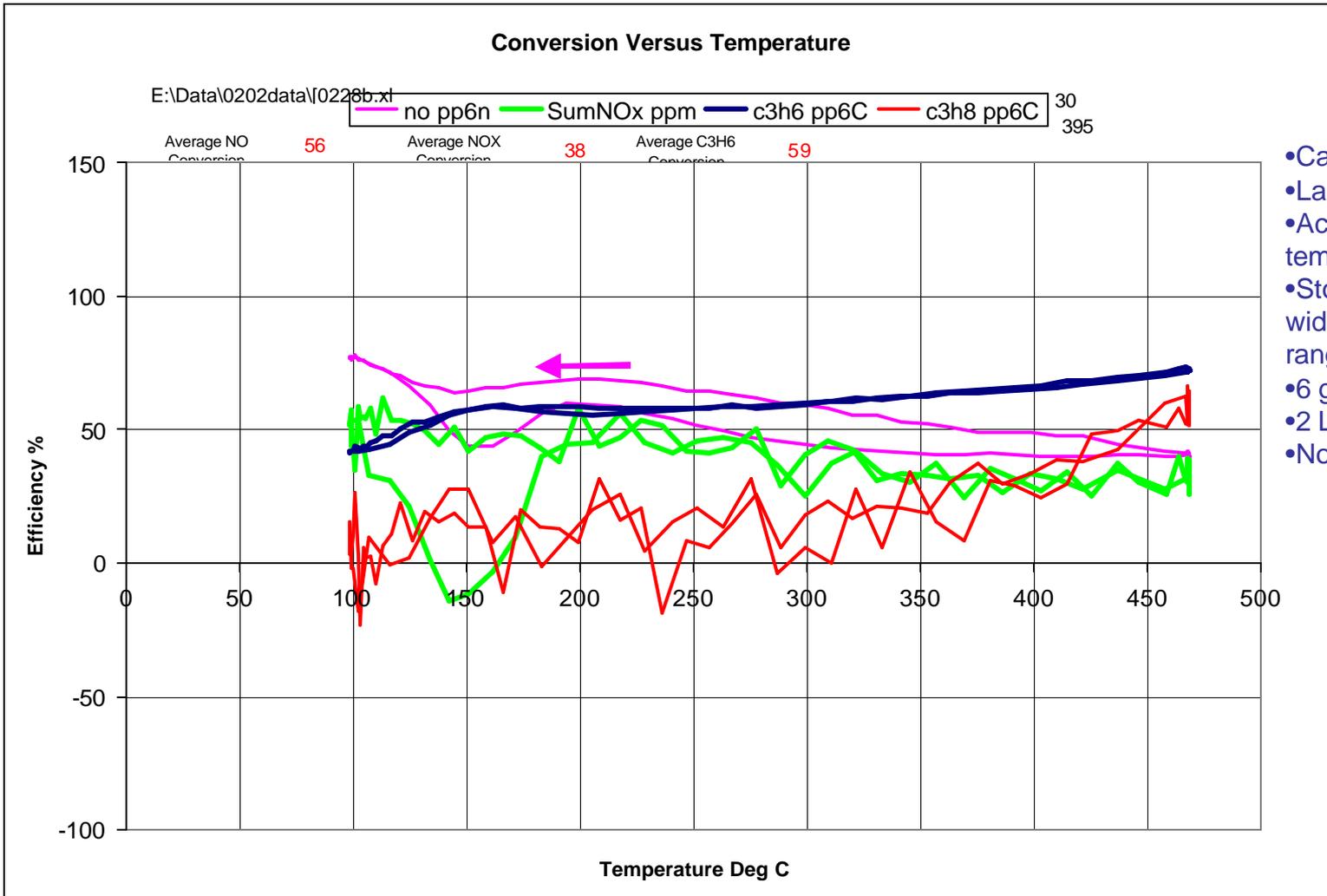
# BaY+ Catalyst



E:\RenoCRADA\SourceFiles\DP\loops.xls]Ef



- BaY with added impregnation
- Data integrated over temperature loops
- 6 grams catalyst
- 4 L/min flow rate
- 50ppm SO<sub>2</sub>



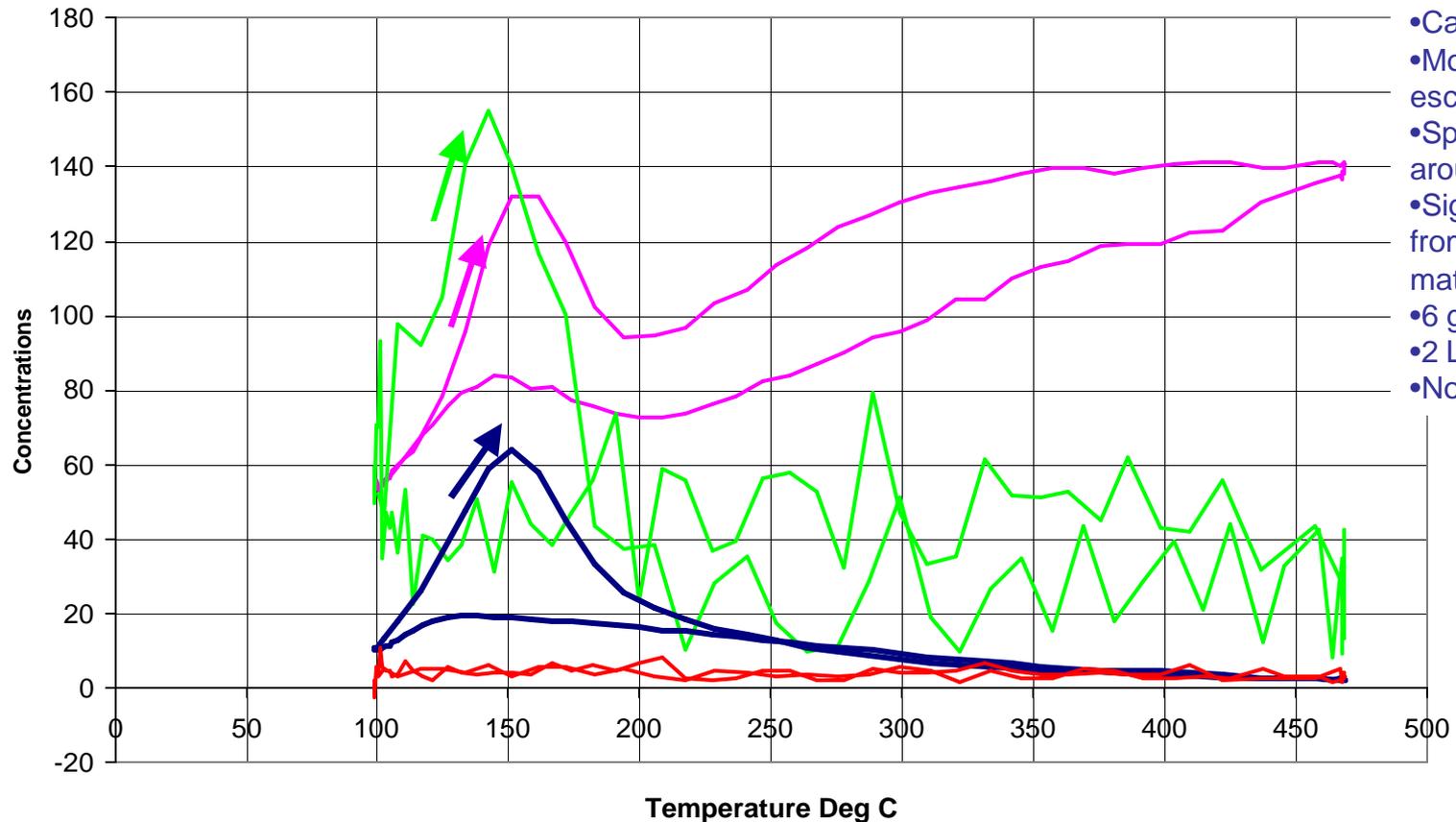
- Catalyst BaY+
- Last loop
- Activity at all temperatures
- Storage over wide temperature range
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

## NOx versus Temperature

E:\Data\0202data\0228b.xl

no pp6n no2 pp6n n2o pp6 hno3 pp6n

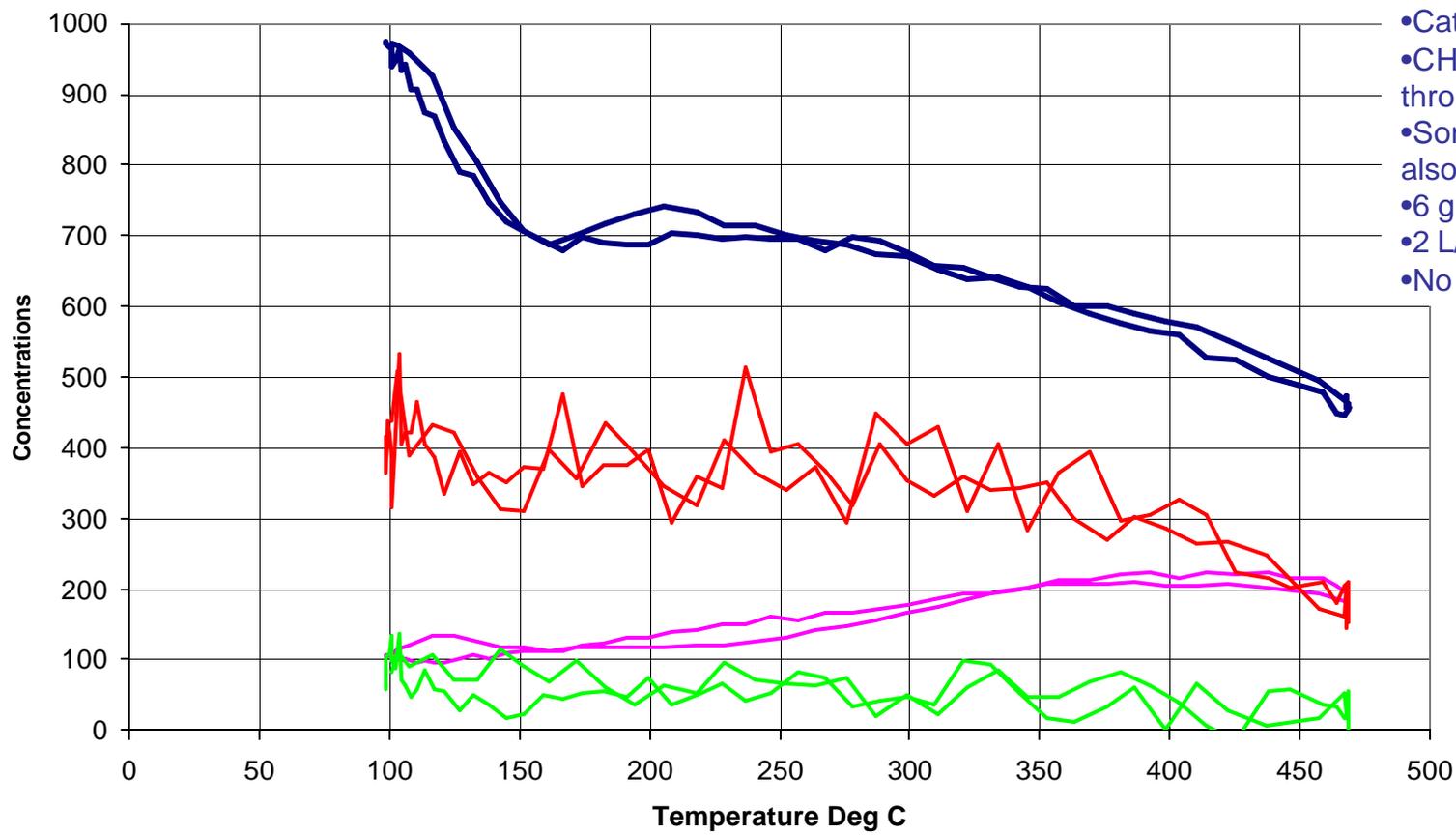
30  
39



- Catalyst BaY+
- Mostly NO escapes
- Spike in NO<sub>2</sub> around 150°C
- Significant N<sub>2</sub>O from stored material
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

### HC and Aldehydes versus Temperature

E:\Data\0202data\0228b.xls  
 ch2o pp6 ch3cho pp6 c3h6 pp6C c3h8 pp6C 30 395



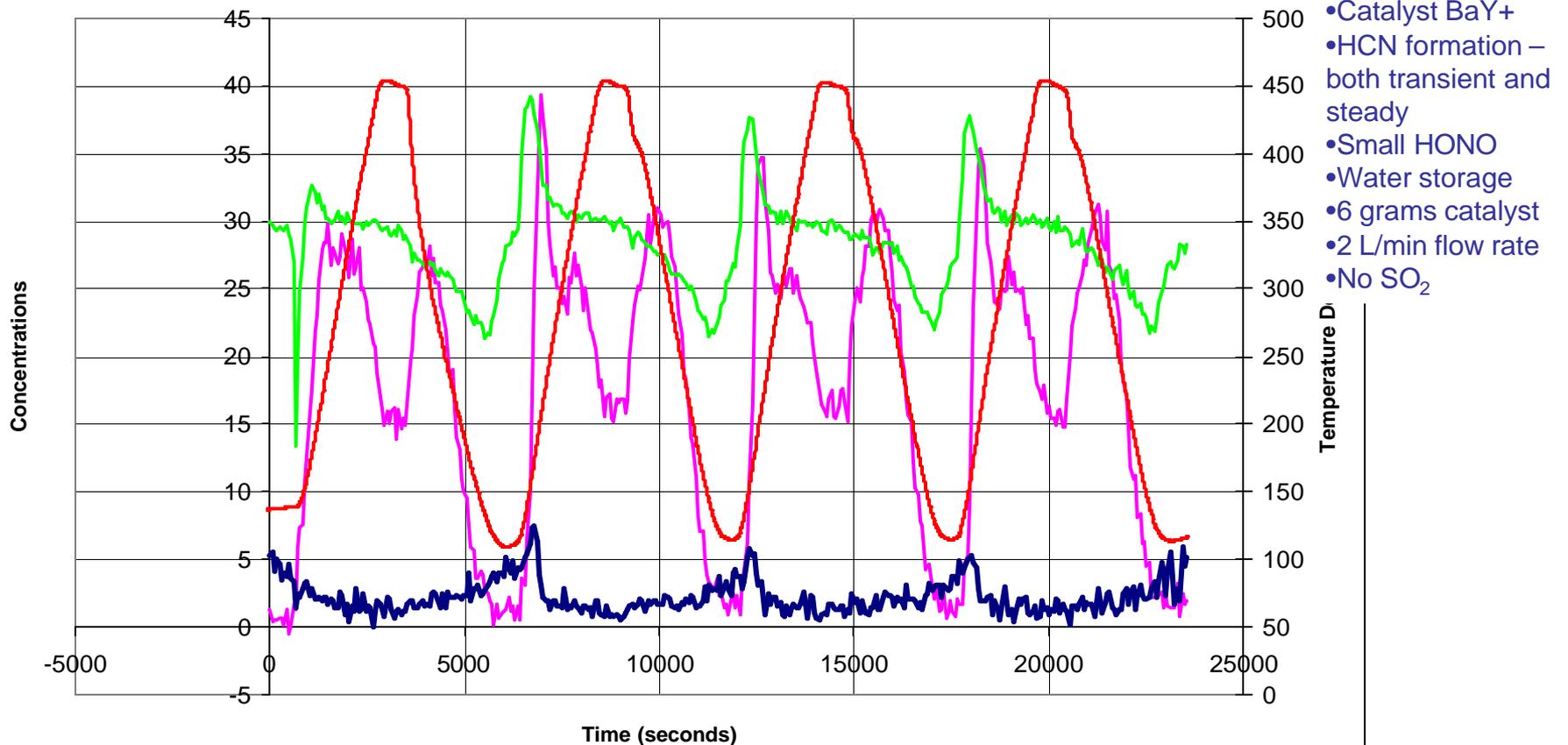
- Catalyst BaY+
- CH<sub>2</sub>O passes through
- Some CH<sub>3</sub>CHO also
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

### Assorted Values Versus Time

E:\Data\0202data\0228b.xl

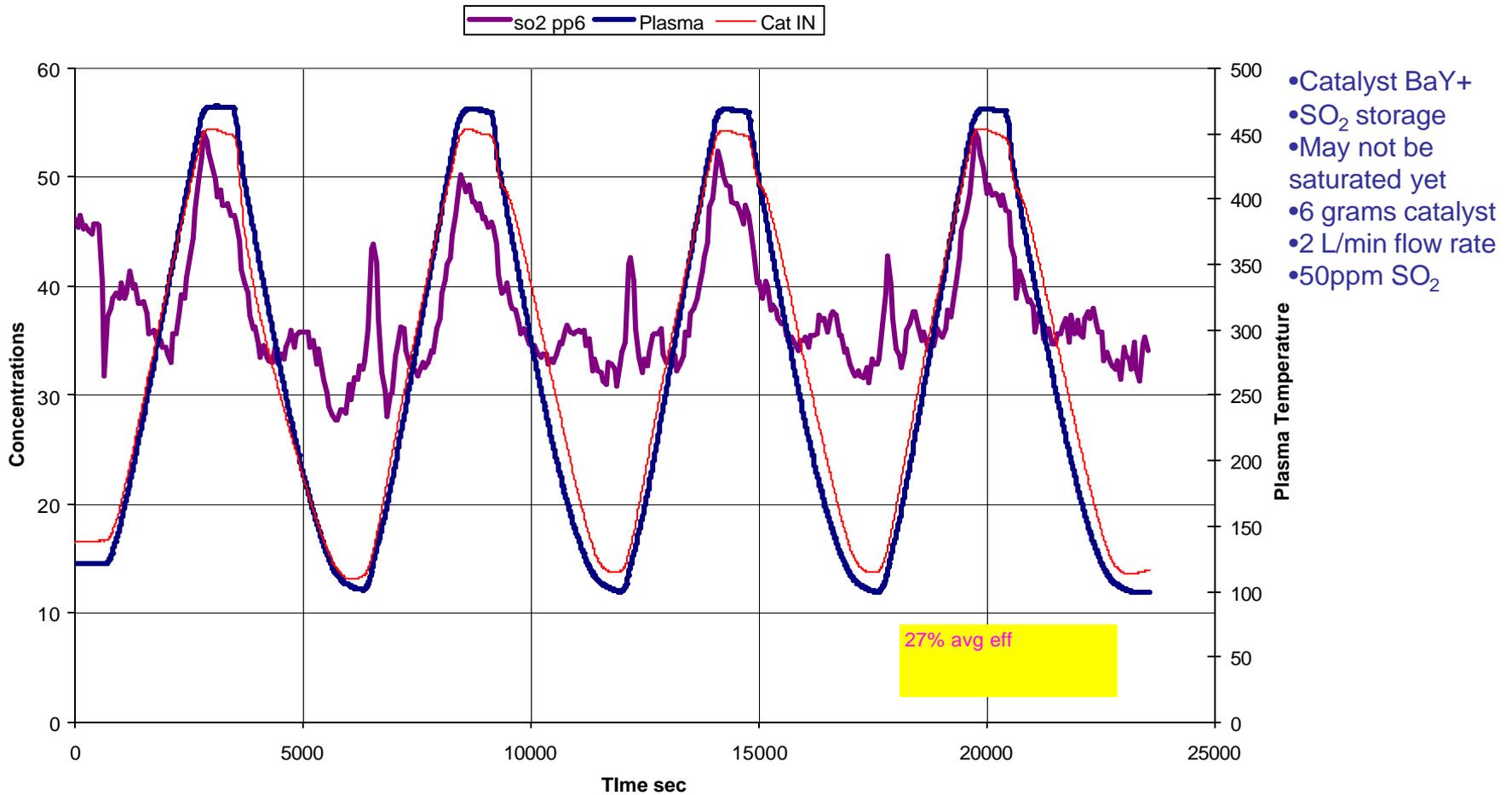
hcn h2o pp3 hono pp6N Cat IN

6  
1000

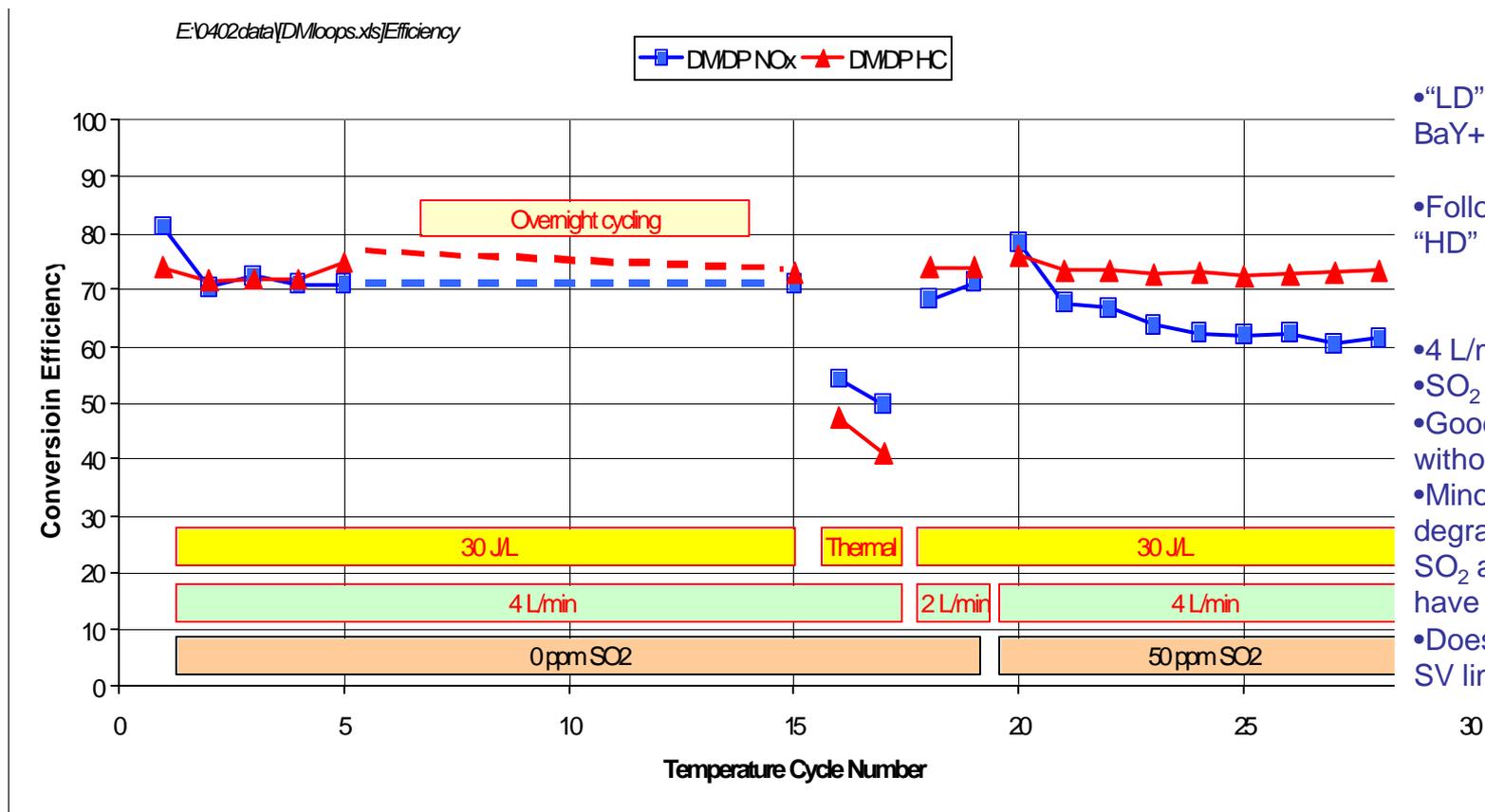


- Catalyst BaY+
- HCN formation – both transient and steady
- Small HONO
- Water storage
- 6 grams catalyst
- 2 L/min flow rate
- No SO<sub>2</sub>

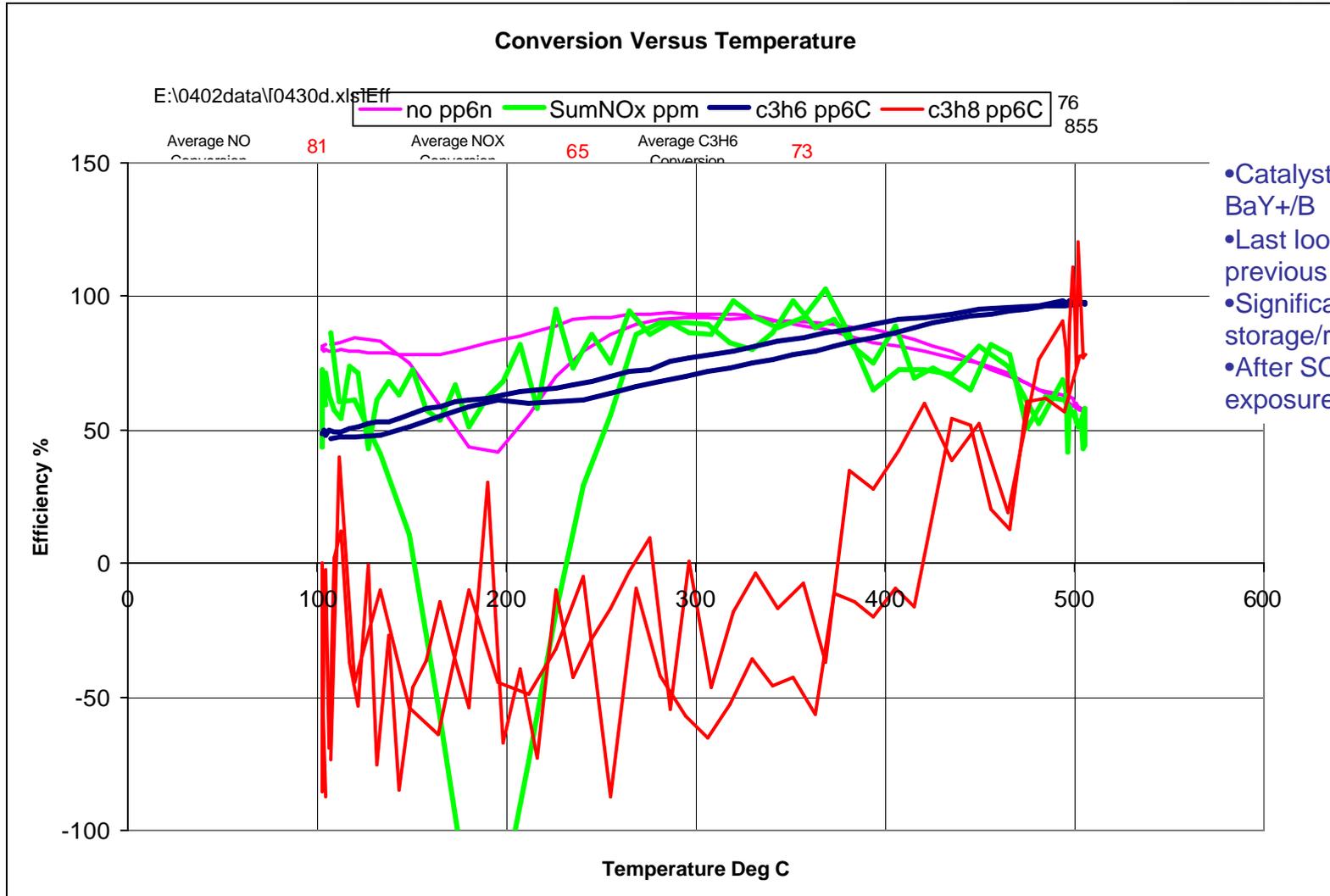
FTIR time series



# Combination: BaY+ / B



- “LD” catalyst BaY+
  - 6 grams
- Followed by “HD” catalyst B
  - 3 grams catalyst
- 4 L/min flow rate
- SO<sub>2</sub> noted
- Good stability without SO<sub>2</sub>
- Minor degradation with SO<sub>2</sub> appears to have stabilized
- Does not appear SV limited

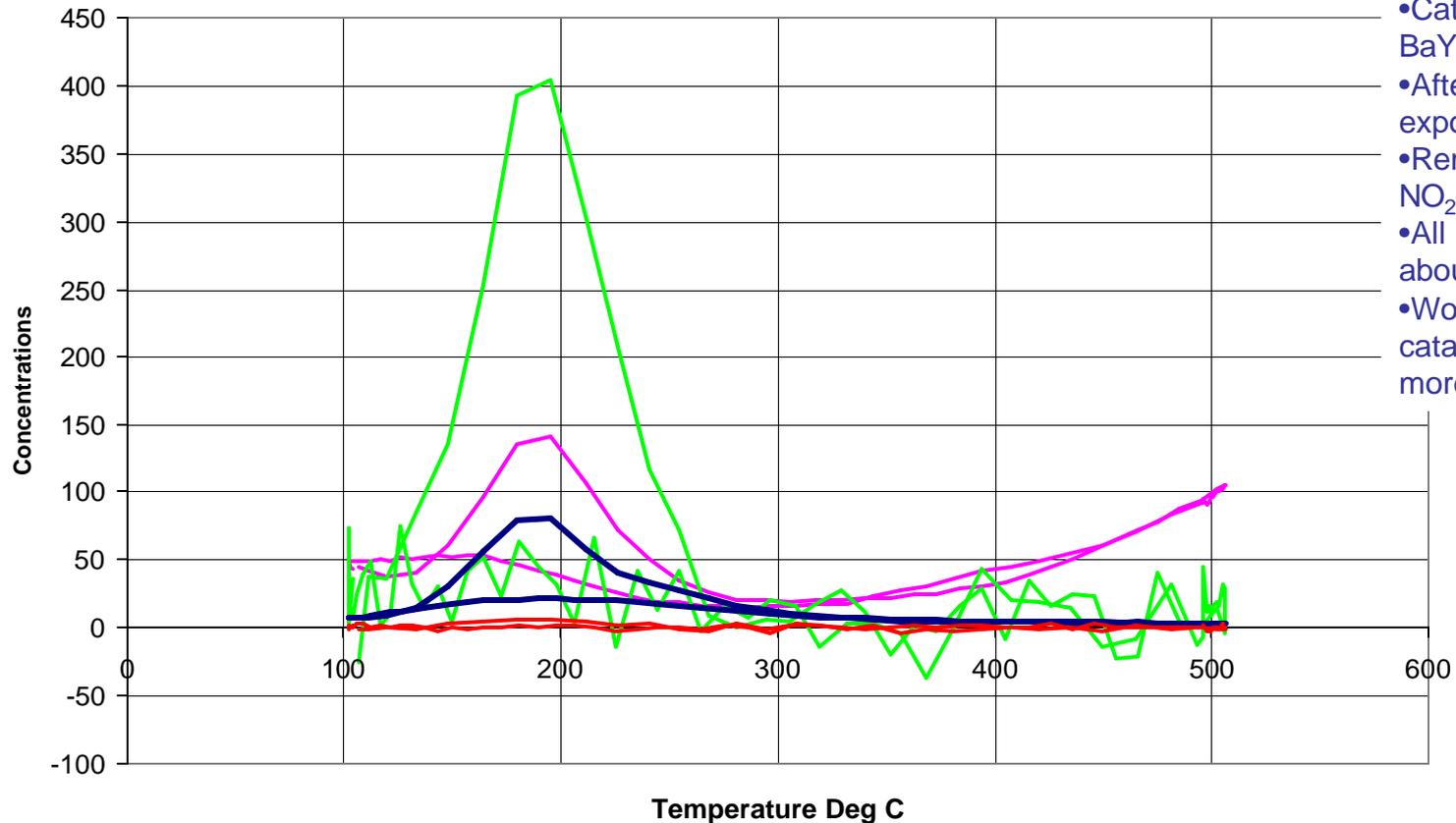


### NOx versus Temperature

E:\0402data\0430d.xls]NO

no pp6n    no2 pp6n    n2o pp6    hno3 pp6n

76  
85

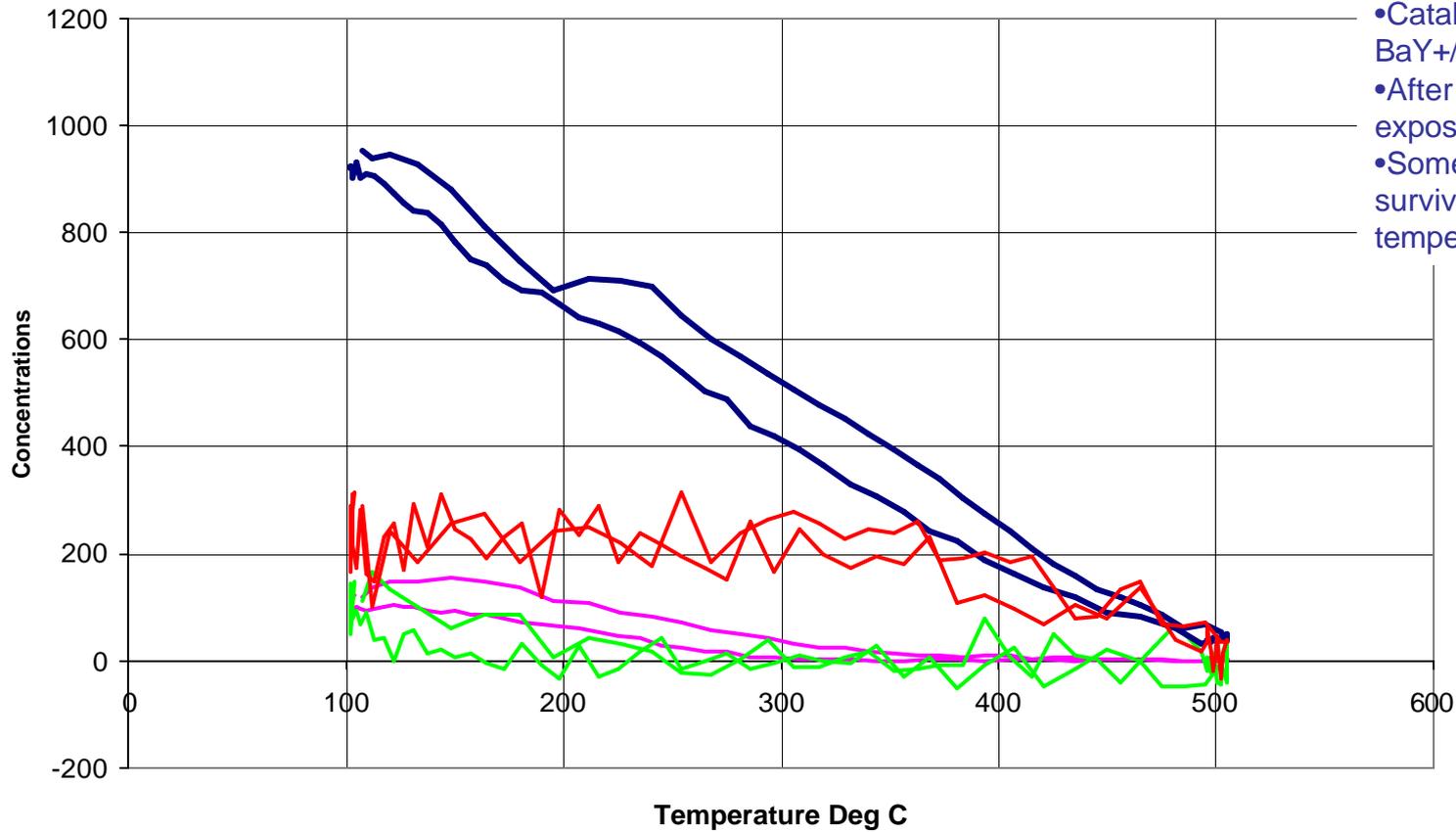


- Catalysts BaY+/B
- After SO<sub>2</sub> exposure
- Remainder is NO<sub>2</sub>, NO, N<sub>2</sub>O
- All released about 180°C
- Would Pt catalyst convert more of this?

## HC and Aldehydes versus Temperature

E:\0402data\0430d.xls HC  
 ch2o pp6 ch3cho pp6 c3h6 pp6C c3h8 pp6C 76 855

- Catalysts BaY+/B
- After SO<sub>2</sub> exposure
- Some aldehydes survive at low temperature

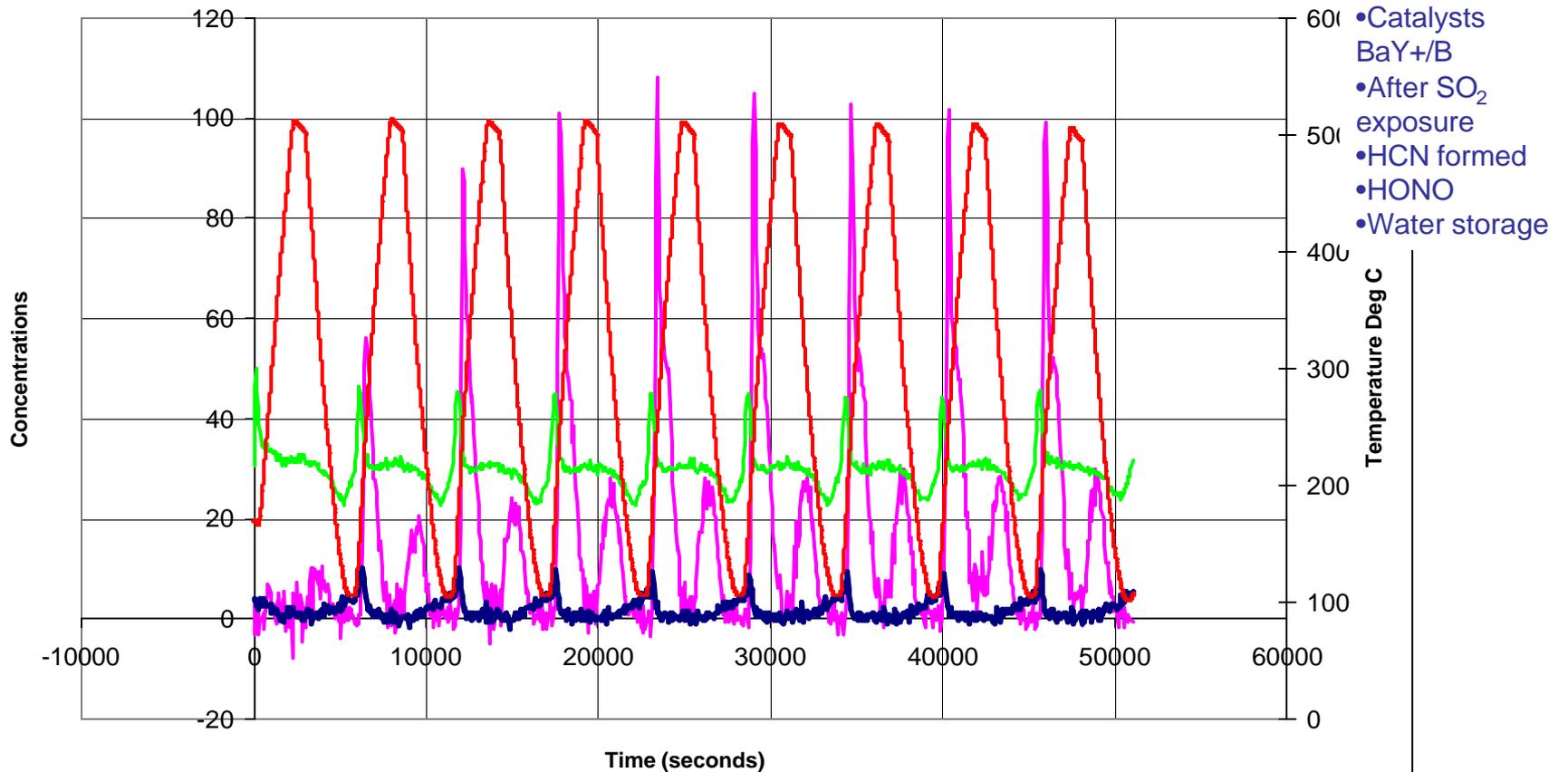


### Assorted Values Versus Time

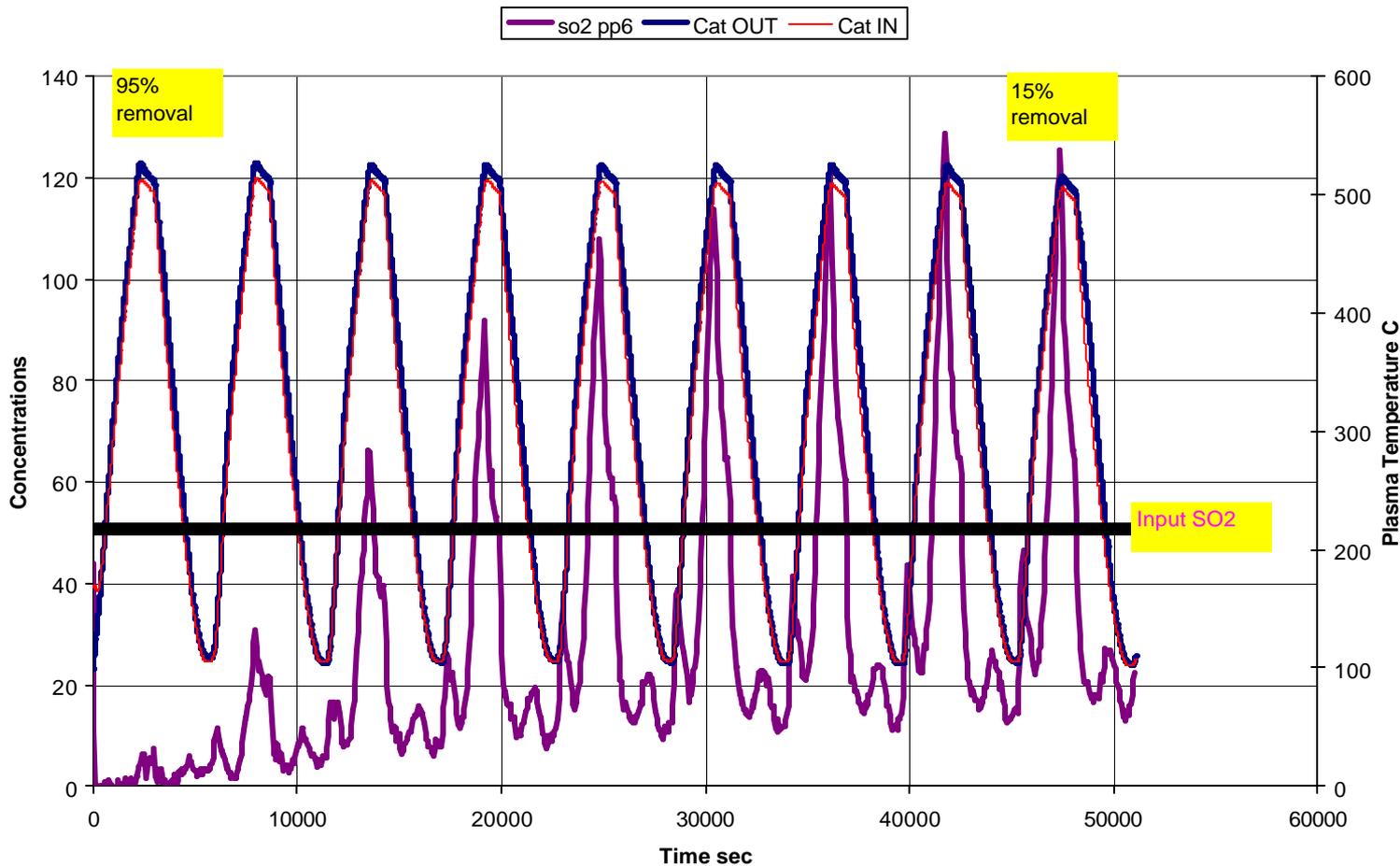
E:\0402data\0430d.xls\Mis

hcn h2o pp3 hono pp6N Cat IN

6  
1000

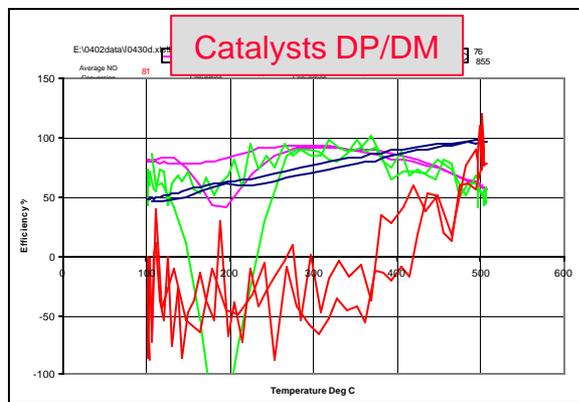
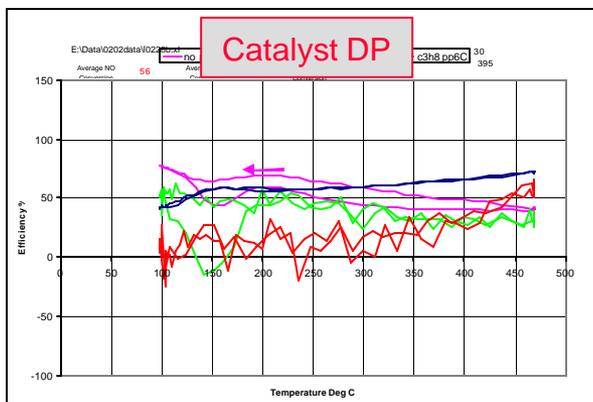
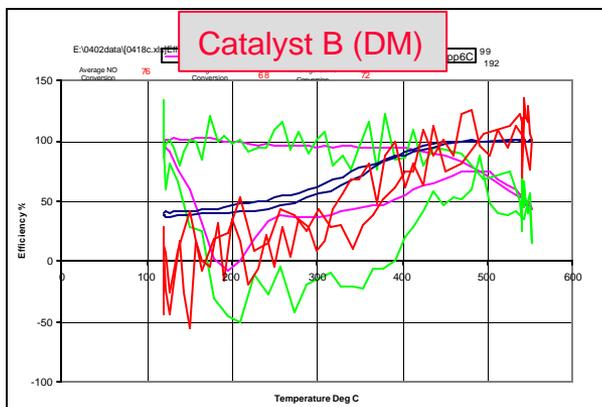


FTIR time series



- Catalysts BaY+/B
- SO<sub>2</sub> adsorption
- Nearly saturated after 9 loops (about 15 hours)
- Low correlation between SO<sub>2</sub> storage and NO<sub>x</sub> conversion
- Some growth in CH<sub>2</sub>O slip at low temperature

# System Comparison



- HD Catalyst B
- 9K SV
- Conversion at high temperature
- Storage at lower temperatures
- LD catalyst DP
- 29K SV
- Lower conversion, wide range of temperature
- Combination DM/DP
- 29.9+42 K SV
- Good conversion over wide temperature range
- Significant storage
- Needs Pt downstream for HC control

# Summary

- Ramp tests are an efficient way to run evaluations and initial aging
  - No known correlation to real world life!
  - Highlight storage/release issues
- Different catalysts have different “slip”
  - NO<sub>x</sub> speciation
  - Aldehyde and HC speciation
  - Temperature ranges
- Combinations can be much superior to single catalysts
  - Wider temperature range
  - Downstream catalyst “catches” slip from upstream
  - Order of catalysts matters; can’t mix them

# Acknowledgements



- This work was performed as part of a CRADA with DOE and PNNL.
- The work was performed at the Ford Research Laboratory.
- Catalyst B was provided by Caterpillar Inc.

